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Corrosion Inhibitive Effects of *Madhuca Longifolia* (ML) on Mild Steel In 1N HCl Solution

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Abstract

The inhibitive action of leaves extract of Madhuca longifolia (ML) on mild steel corrosion in 1N HCl solution was studied using Weight loss method, Potentiodynamic polarization and Electro chemical impedance spectroscopic measurement (EIS). The nature of the protective film on the metal surface has been characterized by scanning Electron microscopy (SEM). Organic moieties present in the extract are found responsible for effective performance of inhibitor which is well supported by FTIR studies. The result obtained showed that the extracts functioned as good inhibitors in HCl solution. Inhibition efficiency was found to increase with increasing concentration of ML extract and reached the maximum of 96 % at 40 ppm.

Keywords: *Corrosion Inhibition; Electrochemical Techniques; Madhuca longifolia (ML); Mild Steel; Scanning Electron Microscopy (SEM); Weight Loss Method.*

1. INTRODUCTION

Mild steel corrosion is a very important phenomenon studied from both theoretical and applicative point of view especially in acidic medium (Srikanth *et al.* 2006). This interest is due to the development of industrial use of acidic solution among which the most important fields are acid descaling, industrial cleaning, acid pickling of steel and ferrous alloys or petrochemical process (Shymala *et al.* 2011). Since mild steel is used under different condition in chemical and allied industries, it encounters severe attack from acid, due to their aggressive nature, resulting in awful degradation (Rajalakshmi *et al.* 2013). Corrosion control of metals is of technical, economical, environmental and aesthetic importance. The use of inhibitor is one amongst the simplest choices of protective metals and alloys against corrosion particularly in acid solution. Corrosion inhibitor is a substance added in small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to it. Large numbers of organic compound have been studied and are still being studied to assess their corrosion inhibition potential. However, most of these substances are not only expensive but also health and environment hazards prompting the search for their replacement.

The plant extracts are considered as an incredibly rich source of environmentally acceptable corrosion inhibitor. A lot of natural products have been previously used as corrosion inhibitor for different metals in various environments (Buchweishaija and Mhinzi, 2008; Abdel-Gaber *et al.* 2006; Raja *et al.* 2008; Farooqi *et al.* 1997). Also plants have been recognized as source of naturally occurring compounds that are generally referred to as "green" compound, some with rather complex molecular structure and having a variety of physical, chemical and biological properties. A number of these compounds are enjoying use in traditional application such as pharmaceuticals and biofuels. Furthermore, there has been a growing trend in the use of natural and medicinal plant used as corrosion inhibitor as they are environmentally safe, readily available and renewable source of a wide range of chemical. Due to biodegradable, eco-friendly, low cost and easily availability, the extract of some common plants based chemical and their by-product have been tried inhibitor for metal under different environment *Madhuca*

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longifolia (ML) is one of the universal plant having medicinal activities. These leaves are expectorant and also used for chronic bronchitis, cushing's disease verminosis, gastropathy, dipsia, consumption, dermatopathy, rheumatism, cephalgia and hemorrhoids.

The present study aims at broadening the application of plant extracts for mild steel corrosion inhibition by investigating the inhibitive properties of ML extract for mild steel corrosion in 1N HCl using weight loss method, potentiodynamic polarization and electrochemical impedance technique.

Fig. 1: *Madhuca longifolia* Leaves

2. MATERIALS & METHODS

2.1 Preparation of Leaves Extract

The leaves of medicinal plants *Madhuca longifolia* collect were taken and cut into small pieces, and they were shade dried in room temperature few days and ground well into powder. From this, 25 g of sample was refluxed in 200 ml distilled water for 3 hrs and kept overnight. The refluxed was then filtered carefully, the filtrate volume was made up to in 500 ml using double distilled water which was the stock solution, and the concentration of the stock solution was expressed in terms of ppm. The extraction value in part per million (ppm) was calculated using the formula:

$$\text{Concentration (ppm)} = \frac{\text{Amount of Solute (mg)}}{\text{Amount of Solvent (liter)}}$$

From the stock solution, 10 - 60 ppm concentration of the extract was prepared using 1N hydrochloric acid. Similar kind of preparation has been reported in studies using aqueous plant extract in the recent years.

2.2 Preparation of Mild Steel Specimen

Mild steel strips containing the composition of (C-0.030 %, Mn-0.169 %, Si-0.015 %, P-0.O31 %, S-0.029 %, Cr-0.029 %, Ni-0.030 %, Mb-0.016 %, Cu-0.017 %) and the reminder Fe, were mechanically cut into 4 cm x 2 cm x 0.1 cm and were used for weight loss studies. The metal specimen were ground successively with (400, 600, 800, 1000, 1200 grade) grit silicon carbide paper (emery paper) followed to achieve mirror finish surface. For electrochemical studies, the mild steel strips of the same composition but with an exposed area of 1 cm^2 were used, subsequently degreased with acetone and finally washed with deionized water, and stored in the desiccators. Accurate weight of the samples was taken using four digit electronic balance model.

3. METHODS

3.1 Weight Loss Methods

Mild steel specimens were immersed in 200 ml of 1N HCl solution containing various concentration of the inhibitor in the absence and presence of mild steel for 24 hrs. The weights of the specimens before and after immersion were determined using four digit model.

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{CR (mmpy)} = \frac{\text{K x Weight loss}}{\text{D x A x t (in hrs)}}$$

where, K = 8.76×10^4 (constant), D is density in gm/cm^3 (7.86), W is weight loss in grams and A is area in cm^2.

The inhibition efficiency (%) was calculated using equation (2) respectively,

$$\text{IE\%} = \frac{W_0 - W_i}{W_0} X100$$

where, W_0 and W_i are the weight loss in the absence and presence of the inhibitor.

3.2 Fourier Transform Infrared (FTIR) Spectrum

FTIR spectra were recorded BRUKER ALPHA 8400S spectrometer. The film was carefully removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

3.3 Potentiodynamic Polarization Method

Potentiodynamic polarization measurements were carried out using CHI608D electrochemical work station analyzer. The polarization measurements were used to evaluate the corrosion current, corrosion potential and Tafel slopes. The experiments were carried out in conventional three electrode cell assembly with working electrode as mild steel specimen 1 cm^2. Platinum electrode was used as counter electrode and calomel electrode was used as reference electrode. A time interval of 10-15 minutes was given for each experiment to attain the study state open circuit potential. The polarization was carried out from cathodic potential to anodic potential at a sweep rate of 1 mV per second. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula:

$$IE\% = \frac{I_{Corr} - I^*_{Corr}}{I_{Corr}} X100$$

Where I_{corr} and I^*_{corr} are corrosion current in the absence and present of inhibitors.

3.4 Electrochemical Impedance Method

The electrochemical AC-impedance measurements were also carried out using CHI608D electrochemical workstation analyzer. Experiments were carried out in three cells assembly as that used for potentiodynamic polarization studies. A sine wave with amplitude 10 mv on the steady state open circuit potential. The real part (z') and the imaginary part (z'') were measured at various frequencies in the range of 100 kHz to 10 MHz. A plot of z' versus z'' was made. From the plot the charge transfer resistance (R_{ct}) was calculated and double layer capacitance (C_{dl}) was calculated using formula:

$$C_{dl} = 1/2\pi f_{max} Rct$$

Where R_{ct} is charge transfer resistance and C_{dl} is double layer capacitance. The experiments were carried out in the absence and presence of different concentration of inhibitor.

$$IE\% = \frac{R_{ct} - R^0_{ct_i}}{R_{ct}} X100$$

Where R_{ct} and R^0_{ct} are the charge resistance values in the inhibited and uninhibited solution respectively.

3.5 Scanning Eletron Microscopy

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of mild steel were examined using (JEOL) computer controlled scanning electron microscope.

3.6 Phytochemical Screening

Phytochemical screening was carried out on the aqueous madhucalongifloia leaves extract freshly prepared according to the common Phytochemical method described earlier (Harborne, 1998). The different chemical constituent tested included alkaloids, terpenoids, sterols, triterpenes, anthraquinones and flavonoids.

4. RESULTS & DISCUSSION

4.1 Weight Loss Method

The weight loss studies were done in 1N hydrochloric acid in the absence and presence of various concentration of the plant extracts ranging from 10 to 60 ppm. Using the weight loss data, corrosion rate, inhibition efficiency, and the optimum concentration of the extract have been calculated. The corrosion parameters obtained in the weight loss method are in table (1). It was observed from the table that the rise in concentration of ML leave extract, on the corrosion rate of mild steel in 1N HCl solution was decreased and the inhibition efficiency increased from 73.98 % to 96.789 % up to 40 ppm. Beyond this concentration, corrosion inhibition efficiency was decreased from 96.789 % to 95.49 %, it indicates that 40ppm is the optimum concentration to get maximum corrosion protection for mild steel in 1N HCl solution using ML leaves extract.

Table 1. Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at different concentration of inhibitor in 1N HCl medium.

Sl.No.	Conc. of solution (ppm)	CR(mmpy)	IE%
1	Blan k	1.8969	-
2	10	0.4434	73.98
3	20	0.1844	90.27
4	30	0.1315	93.06
5	40	0.0589	96.89
6	50	0.0814	95.70
7	60	0.0854	95.49

Immersion Period: 1 day
Inhibitor: *Madhuca longifolia* leaves extract

4.2 FTIR Measurement

FTIR spectra have been used to analyze the protective film formed on metal surface. Lalitha *et al.*

(2005) have confirmed that FTIR spectrometer is a powerful instrument that can be used to determine the type of bonding for organic inhibitor adsorbed on the metal surface. Although various compounds present in the ML leaves extract which contributed in effective working in the inhibitor, It is very difficult to identify each compound separately to know the group present in the ML leaves extracts.

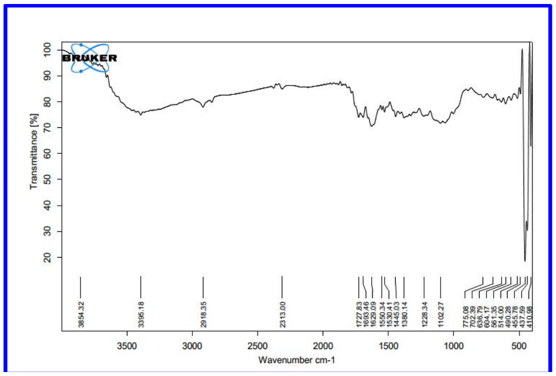

Fig. 2: FTIR Spectra of *Madhuca longifolia* leaves extract

FTIR spectra of the ML leaves extract is shown in Fig. 2. It is observed from the figure, broad peak obtained at 3395.18 cm^{-1} can be assigned to N-H or O-H stretching. C-H stretching was observed at 2918.35 cm^{-1}. Other strong peak obtained at 1727.83 cm^{-1} correspond to C=O (may be aldehyde or ketone). Strong peaks obtained at 1693.46 cm^{-1} and 1629.09 cm^{-1} are due to C=C or C=N stretching or N-H bending vibration. Absorption band at 1445.03 cm^{-1} can be assigned to C-H bending in CH_3 or O-H bending vibration. Peaks observed at 1380.14 cm^{-1}, 1228.34 cm^{-1} and 1102.27 cm^{-1} are due to C-N and C-O stretching vibration. Few weak peaks can also observed at 1550.34 cm^{-1}, 1530.41 cm^{-1}, 1445.03 cm^{-1}, 1380.14 cm^{-1}, 1228.34 cm^{-1} which correspond to C=C stretching vibration of aromatic ring. On the basis of the result, it can be said that ML leaves extract contain Nitrogen and Oxygen (N-H, N=C=S, C=N, C-N, O-H, C=O, C-O) in various functional group and aromatic ring, which make this extract attractive for being used as inhibitor.

4.3 Potentiodynamic Polarization Measurement

Potentiodynamic polarization studies were carried out in CHI-6O8D electrochemical workstation. A three electrode cell assembly was used as work station. The electrochemical parameter like corrosion potential $E_{(corr)}$, corrosion current density $I_{(corr)}$, cathodic Tafel slopes (b_c), anodic Tafel slope (b_a) and percentage of inhibition efficiency for mild steel in the absence and presence of various concentrations of ML extract in 1N HCl is given in Table 2 and their polarization curves are shown in Fig. 3. It is noted from the table that the addition of green inhibitor decreases the dissolution rate of mild steel in 1N HCl acid media. The corrosion current density values decreased considerably for green inhibitor in the acid media. However, the shift in the values of corrosion potential (E_{corr}) for ML leaves extract is not significant This observation clearly showed that the inhibition of mild steel in the presence of the extract control both cathodic and anodic reactions and thus the inhibitor acts like mixed type inhibitors.

Table 2. Electrochemical parameters from polarization measurement, calculated values of inhibition efficiency.

Conc. (ppm)	E_{corr} (mV) vs. SCE	I_{corr}/ (mA/cm^2)	b_c (mV/decade)	b_a (mV/decade)	IE (%)
blank	-474	$3.161x10^{-4}$	108	101	-
10	-476	$0.249x10^{-5}$	103	98	92.09
20	-478	$0.203x10^{-5}$	97	95	93.57
30	-482	$0.172x10^{-5}$	95	93	94.53
40	-505	$0.151x10^{-5}$	98	94	95.23
50	-498	$0.150x10^{-5}$	102	95	95.25
60	-486	$0.118x10^{-5}$	94	94	96.25

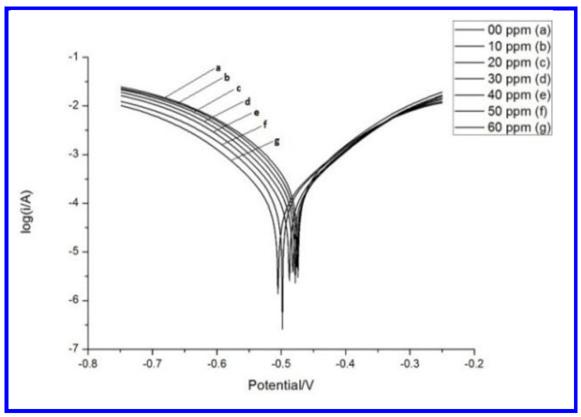

Fig. 3: Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the ansence and presence of different concentration of inhibitor.

4.4 Electrochemical Impedance (EIS) Method

The surface resistances of blank and mild steel specimens with inhibitor in 1N HCl solutions were investigated using EIS techniques. The Nyquist plot of mild steel in 1N HCl in the absence and the presence of various concentration of green inhibitor is shown in Fig. 4. The presence of a single semi circle in the blank and for different concentrations of the inhibitor systems corresponds to the single charge transfer mechanism during dissolution of mild steel,

which is unaltered by the presence of inhibitor components.

The impedance parameters were calculated for mild steel in 1NHCl with and without inhibitors are given in Table 3. The charge transfer resistance (R_{ct}) value calculated for blank Mild steel exhibited 41.76 Ωcm^2 and the double layer capacitance (C_{dl}) was 8.612 $\mu F/cm^2$. When ML leaves extract is added, the R_{ct} value increases from 41.76 Ωcm^2 and C_{dl} value decreases from 8.612 $\mu F/cm^2$. The higher R_{ct} value obtained for higher inhibitor concentration suggests that a protective film is formed on the surface of the metal. The decreased in the C_{dl} values from the blank as the increased in the concentration of the inhibitor confirm the enhancement of the adsorption of the inhibitor on the metal surface. The decrease in C_{dl} is attributed to an increase in thickness of the electronic double layer due to adsorption . The adsorption is due to the electronegative hetero atoms present in the organic constituents of the extract on the electropositive metal surface. All the electrochemical parameters clearly proposed that the corrosion control depends on the concentration of the inhibitor.

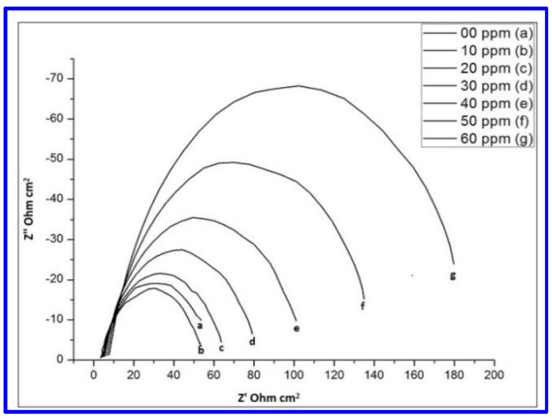

Fig. 4: Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of inhibitor.

4.5 Phytochemical Screening Method

Phytochemical screening of the aerial parts of plant's powder (aqueous) extract was tested in order to find the presence of various chemical constituent included alkaloids, carbohydrates, proteins, saponins, triterpinoids and tannins and the results are listed in Table 4. It is observed from the table that the performed qualitative studies confirmed the presence of alkaloids, carbohydrates, proteins, saponins, triterpinoids and tannins in the aqueous extract of *Madhuca longifolia*. Previous phytochemical studies on *Madhuca longifolia* included characterization of alkaloids, carbohydrates, proteins, saponins, triterpinoids and tannins (Azrakamal, 2014).

Table 3. Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of inhibitor.

S.No	Conc. (ppm)	R_{ct} (ohm cm^2)	C_{dl} (μF/cm^2)	IE (%)
1	Blank	41.76	8.612	-
2	10	43.21	8.397	3.35
3	20	49.56	8.174	15.85
4	30	61.66	8.192	32.27
5	40	78.87	7.974	47.05
6	50	108.0	7.695	61.33
7	60	145.9	7.185	71.37

Table 4. Phytochemical screening of leaves extract of ML

Phytochemical test	Agueous extract
Alkaloids	+
Carbohydrates	+
Proteins	+
Saponins	+
Triterpinoids	+
Tannins	+

4.6 Surface Examination Studies

Scanning electron microscopy was used to examine the morphology of the inhibited mild steel specimens in 1N HCl. SEM images for the mild steel specimens exposed to 1N HCl in the absence and presence of ML extract are shown in Fig. 5 a and b.It should be noted that the mild steel specimen immersed in 1N HCl was rough and highly damaged due to severe attack of aggressive acid. Fig. b clearly showed that a smooth and pits free surface which prevents the metal and inhibiting corrosion (Soror, 2013).

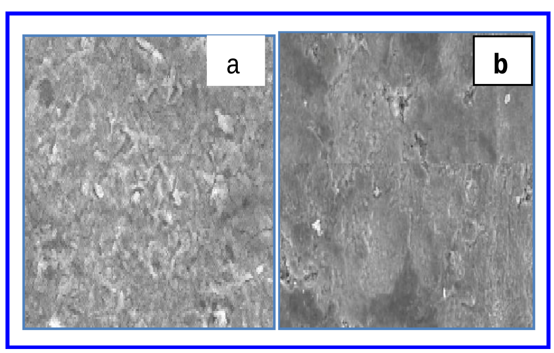

Fig. 5: SEM image of specimen after immersion in 1N HCl acid medium in (a) and (b) absence and presence of inhibitor.

From SEM images, It can be concluded that ML leaves extract inhibited mild steel dissolution in acid by covering the surface area with protective film which has found absent in case of acid interaction with mild steel.

5. CONCLUSION

The effect of various concentrations of *Madhuca longifolia* (ML) leaves extract on the corrosion of mild steel in 1N HCl has been studied. The following conclusion can be made based on the basis of the results obtained.

The *Madhuca longifolia* (ML) leaves extract is a good, easily available and eco-friendly green inhibitor for the corrosion of mild steel in 1N HCl acid solution.

The weight loss data showed that the inhibition efficiency of ML extract increases with increase in the concentration of ML extract and inhibit the corrosion of mild steel at the best concentration of 40ppm.

Polarization studies showed that ML extract acts as mixed type inhibitor and inhibition efficiency increased with the inhibitor concentration.

Protection efficiency of the extract, calculated from EIS was found to increase with increasing in concentration of the inhibitor showing maximum efficiency of 96 % at 40 ppm.

The inhibition efficiencies obtained from polarization, EIS and weight loss measurements are still in acceptable agreement.

SEM examination showed that there was improvement in the surface morphology of the as-corroded inhibited mild steel compared to uninhibited samples.

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